

Stable Isotope Data: Mixed Messages

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Some four decades ago, the author was involved in the study of a Pb-Zn sulfide deposit. Some participants were concerned about the contrasting messages conveyed by the Pb- and S-isotope data. The Pb-isotope data attested to an upper mantle origin whereas the S-isotope data were consistent with reduction of ancient oceanic sulfate with little attending fractionation. It is not uncommon for isotope data of different elements to provide different messages because their geochemical histories may have differed.

However isotopic data from one element may provide seemingly contrasting information as shown in the following examples.

The first example considers investigations of the Quemont ore body in Quebec. In the earlier study of Ryznar *et al*, (1967), the isotopic data were interpreted in terms of kinetic isotope effects during mineralization from an ascending melt. The order of $\delta^{34}\text{S}$ enrichments among the various minerals was not the same as that expected if isotope exchange equilibrium had been approached. However, in a later study (Lusk *et al*, 1975), the order of the $\delta^{34}\text{S}$ values for the minerals was consistent with approaching isotopic equilibrium. Why were the data from the two studies contradictory? In the first study, the massive ore was examined. In the latter, very fine grain mineral occurrences had been sampled. The interiors of the latter could exchange S-isotopes for example with S_2 , closely approaching isotopic equilibrium, but it would be essentially a surface phenomenon with no influence on the interior for the massive deposition.

Evaporites are especially challenging to study as they may have precipitated from brines derived from seawater, continental water, or mixtures of the two. Anhydrites in the Pennsylvanian Watrous and Amaranth Formations of the northern Williston basin were the subject of a recent preliminary investigation by Denison *et al* (2001). The major processes altering the isotope composition of oceanic sulfate are bacterial sulfate reduction (BSR), crystallization of sulfate salts, and inputs from continental sources. The effects of these processes can be shown on a $\delta^{18}\text{O}$ vs $\delta^{34}\text{S}$ diagram (*e.g.*, Krouse, 1987). On this diagram, most data from two wells plotted with slopes near 0.7 and were interpreted as evidence of BSR. However samples from another well plotted with a highly negative slope on the $\delta^{18}\text{O}$ vs $\delta^{34}\text{S}$ diagram. It was subsequently learned from Sr isotope data and other evidence that the lowermost samples were Devonian in age, corresponding to a different evaporite-forming event. Hence any interpretation based on the assumption of one event was invalid.

Samples of polycrystalline PbS from the Bambui Group, Minas Gerais, Brazil were found to vary in $\delta^{34}\text{S}$ value by up to 20‰. One could conclude that this was a low temperature deposit with the large $\delta^{34}\text{S}$ values associated with BSR. One school of thought

considered it to be a Mississippi Valley Type (MVT) deposit. However, when laser bombardment of the surface in an O₂ atmosphere was used to produce SO₂, a more informative observation arose (Li et al, 1996). Earlier deposited PbS had a consistent $\delta^{34}\text{S}$ value near +15‰. Over a depositional increment of only a few mm, the $\delta^{34}\text{S}$ value rapidly increased to over +40‰ and remained at that value during further deposition. This argued for an exhalative scenario with gravitational settling of fine PbS crystals in the water column. The sulfide was a product of BSR. It would appear that at the $\delta^{34}\text{S}$ transition, sulfide was introduced from a sub-basin where sulfate reduction had been more extensive in terms of percent reaction. This implies a radical change in the vent system. Clearly, the large spread in $\delta^{34}\text{S}$ values from random samples arose from varying mixtures of the +15 and +40‰ sulfide.

There are three interpretations for a geothermal system near the ocean having SO₄²⁻ and H₂S with $\delta^{34}\text{S}$ values near +20 and 0‰ respectively.

1. The sulfate was derived from ocean water in the plumbing system whereas the sulfide came from a deep lower crust/magmatic source.
2. The H₂S has a lower $\delta^{34}\text{S}$ value because of kinetic isotope effects (KIE) during sulfate reduction.
3. The isotope distribution represents isotopic equilibration and therefore provides a geothermometer.

The author favours the first interpretation. The rate of exchange of S-isotopes between sulfate and sulfide species is extremely slow. The temperatures of these systems are often too high for BSR but too low for significant thermochemical sulfate reduction (TSR). However any of the above interpretations are difficult to eliminate partly because data from laboratory experiments cannot be reliably extrapolated to *in situ* temperatures. Further, unknown catalysts in the natural system may promote processes which proceed very slowly in the laboratory.

River water represents a challenge for isotopic analyses particularly if there is a smooth bottom. This arises because water flow in streams is dominantly laminar unless there is turbulence produced by rocks, rapids, and falls. Thus, complete transverse mixing of two converging rivers may require distances in excess of 100 km. This was demonstrated for the Liard and Mackenzie Rivers in the NWT, Canada using the oxygen isotope composition of water (Krouse and Mackay, 1971). On a smaller scale, the $\delta^{34}\text{S}$ values of SO₄²⁻ sulfate were found to vary with transverse location in the Bow River in Calgary, Alberta, Canada (Krouse, 1980). Therefore, a requirement for isotopic analyses of river water is a cross-sectional high density sampling grid to check for isotopic uniformity. Lack of isotopic uniformity need not be considered as a liability because it can be used to identify the relative contributions of ions from different sources.

Data for KIEs during laboratory chemical and bacterial conversions are often misleading. Historically, the product after a low percentage reaction would be compared isotopically to the starting material and this was assumed to represent the KIE. This was correct if the reaction reached steady state conditions immediately, *i.e.*, the slowest step achieved rate control. However, it can be shown mathematically that for 1st order reaction steps, the

isotope fractionation near zero percent reaction is the product of the KIEs in all steps (Rees, 1973). This was demonstrated convincingly with Se isotopes during chemical selenite reduction (Rashid and Krouse, 1985). The data were consistent with two steps competing for rate control over a considerable extent of the reaction before one step emerged as the victor.

Earlier isotope fractionation data from bacterial conversions were often obtained under non-steady state conditions even if the reaction mixture was added to a large culture that had reached a steady state population. If a small culture is added to the reaction mixture, the isotopic fractionation behaves erratically particularly during the growth phase. During sulfate, sulfite, nitrate, and nitrite reductions, the isotope discrimination is much smaller at low percent conversions (e.g., Smejkal *et al*, 1971; McCready *et al*, 1975; Wellman *et al*, 1968; Cook *et al*, 1970). Even more spectacular was the “inverse” apparent KIE found during sulfite reduction by *Clostridium pasteurianum* (e.g., McCready *et al*, 1975). Evolved H₂S became very enriched in ³⁴S compared to the reaction/intermediates mixture in the reaction flask. A pronounced positive “spike” in $\delta^{34}\text{S}$ value of the H₂S occurred at about 50 percent generation of product. This phenomenon could be explained in terms of the reaction splitting into two parallel paths with quite different rate constants and both pathways giving rise to the same final product (Laishley *et al*, 1975).

In the examples above, steady state conditions were not reached over much or even all of the conversion. Stating it another way, the isotopic composition of the final product was not consistent with that of the disappearing reactant. Realizing this, the author was perhaps the first to advocate that isotope fractionation studies of chemical and bacterial conversions should include taking as many samples as feasible throughout the duration of the reaction (Rees, 1973).

Mixed messages in environmental stable isotope investigations can readily arise. In a study of the effects of SO₂ emissions from a sour (H₂S –rich) gas processing plant, the $\delta^{34}\text{S}$ data for vegetation were not consistent with variables such as concentrations and biological stress indicators. One could conclude that the S-isotope data were worthless. It was finally realized that the $\delta^{34}\text{S}$ values correlated with elevation and the “mystery” was solved (Krouse, 1991). Natural sulfate had been leached by groundwater from knolls into depressions where vegetation was S-stressed. Trees on knolls actually benefited by the uptake of atmospheric SO₂ since the leached soil was sulfate-poor.

In another unpublished study near a sour gas plant, grass was found to have positive $\delta^{34}\text{S}$ values near that of atmospheric SO₂ whereas the leaves of adjacent thistles had a very high S-content (over 10,000 ppm) with very negative $\delta^{34}\text{S}$ values. The mixed message is readily solved. The grass had shallow roots in soil that was sulfate-poor. The deep roots of the thistle reached the C- horizon which had high concentrations of sulfate with negative $\delta^{34}\text{S}$ values.

Many other examples of mixed messages from stable isotope data can be cited for geological systems, ecosystems, and laboratory conversions. They invariably convey information and the problem is to recognize it. Perhaps

1. the researcher did not pose the correct question
2. the sampling design was inadequate
3. not enough parameters were measured to adequately characterize the samples.

With the recent advancements in isotopic analyses of samples of a few micrograms, previous mixed messages have sometimes become clear. The tendency to examine many components and measuring many parameters in a system has reduced the incidence of mixed messages. Better sampling resolution is desirable in terms of time, space, and chemical/physical composition. For example, it is not adequate to measure the total $\delta^{34}\text{S}$ value for a bitumen when different organic –S compounds within it may vary widely in S-isotope composition (Krouse *et al*, 1987).

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